NASA TECHNICAL MEMORANDUM

NASA TM X-52184

RETENTION OF FUEL IN TUNGSTEN-URANIUM DIOXIDE FUEL ELEMENTS (U)

by Neal T. Saunders, Michael A. Gedwill,
and Richard E. Gluyas
Lewis Research Center
Cleveland, Ohio

CLASSIFICATION CHANGE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION · WASHINGTON, D.C. · 1966

C66-2785

RETENTION OF FUEL IN TUNGSTEN-URANIUM

DIOXIDE FUEL ELEMENTS (U)

by Neal T. Saunders, Michael A. Gedwill, and Richard E. Gluyas

Lewis Research Center
Cleveland, Ohio

TECHNICAL PAPER presented at

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

RETENTION OF FUEL IN TUNGSTEN-URANIUM DIOXIDE FUEL ELEMENTS (U)

by Neal T. Saunders, Michael A. Gedwill,
and Richard E. Gluyas

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio

I. INTRODUCTION

A tungsten, water-moderated, nuclear reactor concept is currently being considered by NASA for space propulsion. This reactor (described in Ref. 1) would use fuel elements consisting of uranium dioxide (UO_2) particles dispersed in a continuous tungsten (W) matrix. Since the reactor would operate in the thermal neutron spectrum at temperatures to at least 4500° F, relatively low fuel loadings (10 to 35 volume % UO_2) are being considered. These low fuel loadings allow maximum utilization of the good high-temperature strength and thermal conductivity of W..

One of the major problem areas associated with the use of W-UO_2 fuel elements in this type of reactor is the possible loss of fuel during high-temperature operation. This problem stems primarily from two different causes:

1) the high vapor pressure of UO_2 at elevated temperatures, and

2) the decomposition of UO_2 at elevated temperatures and the subsequent precipitation of U at lower temperatures, which

  leads to the cracking of the W matrix along the grain boundaries.

These causes are somewhat interrelated because fuel loss through the cracked grain boundaries in the second case eventually occurs by vaporization. However, the two causes can be studied independently since

vaporization losses can be evaluated under constant (noncyclic) heating conditions while the destructive effects of fuel decomposition are predominant under thermal cycling conditions. Combination of the solutions resulting from independent study of these effects should lead to improved fuel retention capabilities for W-UO_2 composites.

A program is being conducted at Lewis to study both aspects of the fuel retention problem. Earlier results from these studies are reported in Ref. 2, and the more recent results obtained from this continuing program are reported herein.

II. FUEL VAPORIZATION

Since UO_2 has a relatively high vapor pressure at elevated temperatures (e.g., approximately 3 mm of Hg at 4500° F), any UO_2 exposed to rocket reactor atmospheres (such as the vacuum of space or the gaseous hydrogen propellant) will vaporize at high temperatures. Under these conditions, surface fuel particles in W-UO_2 composites can vaporize away from the composites, and eventually, adjacent, interconnected particles will be lost from within the composites. As discussed in Ref. 2, two different methods have been found to be effective in reducing this type of fuel loss. One method involves cladding of the surfaces of the composites with a thin (approximately 0.001 in.) layer of unfueled W. The other method depends upon preventing interconnection of the UO_2 particles within the composites by precoating the individual fuel particles with W prior to their consolidation into bodies. Both of these methods of fuel retention are currently being studied.

A. Surface Cladding

For maximum effectiveness, surface claddings must be highly dense and must be metallurgically bonded to the W matrix of the fueled core. One method (described in Ref. 3) of meeting these requirements involves application of claddings to the top and bottom surfaces of flat plates by roll-bonding of thin, wrought W foil during a hot-rolling process that is used to increase the density of composites. This method has proven quite useful since high quality cladding can be easily bonded to the major surfaces of fueled cores. Therefore, most of the clad test specimens used in these studies have utilized this type of cladding.

Because roll-bonded claddings on the two major surfaces do not prevent loss of some fuel through the exposed edges of fueled composites, other types of claddings are required for use either in conjunction with or in place of roll-bonded W foil. Three methods of cladding which appear quite promising are: plasma spraying of W powders; pressure bonding of W foil; and vapor deposition of W by hydrogen reduction of W halides.

The three different methods of applying claddings are all being studied because of their usefulness in different applications. For example, plasma spraying (although possibly useful for cladding entire surfaces) appears to be most useful either for edge cladding of roll-clad plates or for repairing defects in other types of cladding that

might be caused by handling or machining of fuel element components. Pressure bonding of foil appears to be the best method of producing high quality claddings of uniform thickness, but this method of cladding is difficult to apply to complex fuel element configurations. Vapor deposition, on the other hand, is not as geometrically limited, but is more difficult to control and to attain uniform cladding thicknesses.

The effectiveness of all of these methods of applying surface claddings has been demonstrated in numerous high-temperature tests. For example, 2-hour fuel loss tests in flowing hydrogen at 4500° F have indicated that less than 1 weight % of the fuel is lost from thin 80 volume % W + 20 volume % UO_2 composites that were surface clad by any of the three cladding methods being studied, while similar unclad specimens lost about 18 weight % UO_2 under the same test conditions. An example of a 80 volume % W + 20 volume % UO_2 composite that was surface-clad by vapor deposition is shown in Fig. 1. This composite was tested for 2 hours at 4500° F prior to sectioning, and it is apparent that the thin W cladding effectively prevented loss of the fuel.

B. Coated Particles

Although thin surface claddings can be highly effective in retaining the fuel in W-UO_2 composites, the necessity for assuring good bonding increases the problems in both fabrication and inspection of complex fuel element configurations. Because of this, the alternate method of precoating individual UO_2 particles prior to consolidation is also being studied.

Development of this method of reducing fuel vaporization losses has been hindered by difficulties encountered in coating of the particles and in consolidation of the particles into dense composites, but solutions to these problems are being developed. A major problem associated with the particle coating process has been contamination of the particles with fluoride impurities as a result of the WF_6 vapor deposition process usually used to coat the particles. The reaction of the UO_2 with the HF generated in the deposition process has resulted in fluoride contents of from 150 to 3000 parts per million by weight (ppm). However, some suppliers are now avoiding this fluoride contamination problem by using hydrogen reduction of WCl_6 because the HCl generated does not readily react with UO_2. Use of this process has resulted in particles (see Fig. 2(a)) containing less than 50 ppm of all halides. Consolidation of the relatively large (about 60μ diameter) coated UO_2 particles into dense composites has also presented fabrication difficulties, but recent developments in several fabrication processes have resulted in composites with densities greater than 98% of theoretical. The most promising processes for consolidating these particles involve hot compaction in molybdenum containers by rolling, isostatic pressing, or pneumatic impaction.

With these recent improvements in particle coating and consolidation techniques, high quality W-UO_2 composites are now being produced from coated particles, and fuel retention tests are being initiated to

determine the usefulness of this fuel retention method. The initial

data from 80 volume % W + 20 volume % UO_2 composites that were consolidated

by roll-compaction and tested at 4500° F in H_2 indicate a fuel loss of

2.6 weight % in 2 hours. Metallographic examination of these composites

(see Fig. 2(b)) indicated that this measured weight loss was due

entirely to the loss of fuel particles adjacent to the surfaces and that

the W barriers between the particles had effectively prevented loss of

internal particles. Since the roll-compaction process produced considerable

deformation of the particles, the loss of the surface particles is due,

in part, to cracking of the coatings on the surface particles during

consolidation. Therefore, consolidation processes that involve less

severe particle deformation should lead to even lower fuel losses.

C. Comparison of Surface Cladding and Coated Particles

Although both surface cladding and precoating of the fuel particles

are effective in reducing UO_2 vaporization losses from W-UO_2 composites,

the results of fuel retention tests conducted to date indicate that

surface claddings are somewhat more effective in retaining fuel.

However, the technology of producing and consolidating coated particles

is not as far advanced as that of surface cladding methods. In addition,

the small amount of fuel loss that is associated with loss of some sur-

face particles in composites produced from coated particles is con-

sidered tolerable for reactor use. Since the use of coated particles

has the advantages of producing more uniform fuel dispersions and of

reducing nondestructive testing requirements (i.e., inspection of core-to-clad bonds is not required), W coating of UO_2 particles is considered to be the prime method for reducing fuel vaporization from $W-UO_2$ fuel elements. However, for additional reliability, it may be desirable to utilize both coated particles and surface claddings to minimize fuel vaporization.

III. FUEL DECOMPOSITION

As described in Ref. 2, slight decomposition of UO_2 at elevated temperatures can present a serious fuel retention problem under thermal cycling conditions such as those that would be encountered in successive startups and shutdowns of the reactor. This problem stems from the fact that UO_2 has a range of solubilities for both U and O_2 at elevated temperatures. Therefore, at the high reactor operating temperatures, UO_2 particles encapsulated in a W matrix can change in composition by losing O_2 to the matrix and subsequently precipitating excess U at lower temperatures. Migration of the U through the W matrix can result in gross deterioration of the composites and a rapid loss of fuel.

A. Effects of Cycling Variables

Results of extensive studies of this problem (Ref. 4) indicate that the thermal cycling conditions can greatly affect the rate of fuel loss. Increasing the maximum temperature, the number of cycles, and/or the duration of cycles can cause an increase in the rate of fuel loss per cycle from the composites. The fuel loss rate is also greatly

accelerated by cycling in a hydrogen atmosphere rather than in vacuo

or in an inert atmosphere. Two other important cycling test variables

currently being investigated are the flow rate and pressure of the test

atmosphere. A slowly flowing (35 scfh) hydrogen atmosphere presents a

more critical test than a nonflowing atmosphere, probably due to

accumulation in the latter of reaction products resulting from hydrogen

reduction of UO_2. However, the effects of the high hydrogen gas pres-

sures and flow rates expected in reactor operations are as yet unknown.

The independent and combined effects of these two variables are being

evaluated in a fuel element test facility recently installed at Lewis.

Because of the influence of testing variables, a standard set of

cyclic test conditions was established for testing of the various

composites discussed in the following paragraphs. These conditions were

chosen to simulate the reactor operating conditions as closely as

possible in a laboratory test. The test conditions involve thermal

cycling of specimens between ambient temperature and 4500° F in a

flowing hydrogen atmosphere (35 scfh at atmospheric pressure). The

specimens are heated and cooled in less than 2 minutes while the hold

time at temperature for each cycle is 10 minutes. Weight changes are

usually measured after each 5 cycles.

Using this set of cycling conditions, a series of $W-UO_2$ composites

with varying fuel loadings was tested. These thin, rectangular specimens

(and all subsequently described specimens) were fabricated by the

sintering and hot-rolling process described in Ref. 3, and were surface clad on the two major surfaces by roll-cladding with W foil. The fuel loss data resulting from this series of tests are summarized in Fig. 3. These plots indicate that increases in fuel loading greatly increase the rate of fuel loss from the composites. This change in fuel loss rate (which was much greater than that anticipated) is probably due to the greater amount of fuel being reduced and the greater contact and interaction of fuel particles in the composites with the higher fuel loadings. Since the higher fuel loadings are more critical under these test conditions, most of this type of testing has been performed on composites with the higher range of fuel loadings of interest for reactor use -- 20 and 35 volume % UO_2.

B. Possible Solutions

Considerable effort has been expended in attempting to understand the cause and in seeking solutions for the thermal cycling effect. While this phenomena is not yet completely understood, test results (described in Ref. 4) indicate that the detrimental effect can be reduced by at least three different methods. These are (listed in order of increasing effectiveness):

(1) additions of small amounts of fine thorium dioxide (thoria, ThO_2) particles to the W matrix;

(2) use of fine (about 1μ) UO_2 particles instead of the larger (about 50μ) fuel particles; and/or

(3) additions of metal oxide additives in solid solution with the UO_2. The effectiveness of the first two methods is indicated in the fuel loss plots shown in Fig. 4. These plots demonstrate that additions of 2 volume % fine ThO_2 particles are at least partially effective in prolonging the cyclic lifetime of W-UO_2 composites, but that the thoriated composites do not meet the established goal of 5 weight % maximum fuel loss after 25 cycles. On the other hand, use of fine UO_2 particles in the composites resulted in cyclic lifetimes that could possibly be considered for reactor use. Unfortunately, use of the fine UO_2 particles results in an appreciable reduction in strength of the composites. In addition, it is extremely difficult to tungsten-coat the fine fuel particles. Therefore, this method of reducing the effects of thermal cycling is not considered a prime method at this time.

Currently, the most promising method of reducing fuel decomposition is through the addition of other metal oxides to the UO_2. This method apparently is effective because it stabilizes the fuel by reducing the oxygen activity of the fuel and thus reduces the amount of UO_2 reduction. The initial studies of this method of fuel stabilization used 10 mole % additions of zirconia (ZrO_2), thoria (ThO_2), and calcia (CaO). The results of this study (reported in Ref. 5) indicated that CaO additions were the most effective of these in reducing fuel loss from partially clad (major surfaces clad but edges unclad) 80 volume % W + 20 volume % UO_2 composites. More recent studies (reported in Ref. 6) involved compari-

son of the effectiveness of CaO or yttria (Y_2O_3) additions in <u>fully clad</u>
composites. The results of this latter study are summarized in Fig. 5.
These plots compare the amount of fuel loss from composites containing
either 20 or 35 volume % fuel with 10 mole % of the additives in the
UO_2. These plots indicate that both CaO and Y_2O_3 additions are effective
in prolonging the cyclic life, but that Y_2O_3 additions are the more
effective.

Although the plots shown in Fig. 5 indicate that either CaO or
Y_2O_3 additions could be used to stabilize the composites for up to
25 cycles, metallographic examination of samples that were subjected to
25 cycles indicates that weight loss measurements do not fully describe
the stability of composites. Photomicrographs of tested composites con-
taining either CaO or Y_2O_3 in the fuel are shown for comparison in Fig. 6.
Appreciable fuel migration along tungsten grain boundaries had occurred
in the sample that contained CaO additions, but no appreciable migration
is evident in the Y_2O_3 stabilized composite. The fuel migration through
the W grain boundaries of the calciated composite would be expected to
decrease the strength of this material. Based on these observations,
Y_2O_3 additions are currently considered the more promising for reactor use.

Although Y_2O_3 stabilized composites appear suitable for use, the
large increase in ceramic phase associated with 10 mole % additions
(e.g., 10 mole % Y_2O_3 additions results in a ceramic phase of about
42 volume % in a W-UO_2 composite with a fuel loading equivalent to 35 volume %

UO_2) could cause an appreciable decrease in the strengths of the composites, particularly at the higher reactor fuel loadings. Data reported in Ref. 7 indicates that the ultimate tensile strength of $W-UO_2$ composites at 4500° F decreases rapidly at fuel loadings greater than about 30 volume %. Therefore, studies are now being made to determine if lower amounts of Y_2O_3 are as satisfactory and if other metal oxide additions are as good or even more effective than Y_2O_3 additions.

Initial studies (reported in Ref. 6) on the effects of lower additions of Y_2O_3 utilized additions of 2.5, 5, and 10 mole %. The data obtained from these tests are plotted in Fig. 7. These plots indicate that additions of at least 5 mole % are needed in order to assume that appreciable migration of the fuel does not occur within 25 cycles, but further study of the effects of varying amounts of Y_2O_3 additions are needed to better define the minimum amounts required for adequate fuel stabilization.

Initial screening tests on the relative effectiveness of other metal-oxide additions has included study of the following oxides: strontium oxide (SrO), magnesium oxide (MgO), neodymium oxide (Nd_2O_3), cerium oxide (CeO_2), and praseodymium oxide (PrO_2). These oxides were selected on the basis of their apparent solubilities in UO_2 (based on considerations of ionic radii), their valencies, and their low thermal neutron cross sections (needed for use in a thermal reactor). Results of cyclic tests on _partially-clad_ W + 35 volume % UO_2, composites containing

10 mole % of the additives indicated that the effectiveness of these

additives generally fall into the three following groups:

(1) additions of SrO and MgO yielded fuel loss results similar to

those obtained with CaO additions;

(2) additions of Nd_2O_3 were about as effective as those of Y_2O_3, and

(3) additons of PrO_2 and CeO_2 were even more effective than Y_2O_3

additions.

Additions of Nd_2O_3 and Y_2O_3 are thought to be effective in stabilizing

UO_2 because they form a vacancy-defect, fluorite-type lattice with UO_2

that is more difficult to reduce than the unaltered UO_2 lattice (as

described in Ref. 6). The possible greater stability of UO_2 with PrO_2

or CeO_2 is thought to be associated with the reduction of these metal

oxides to Pr_2O_3 or Ce_2O_3, respectively, at elevated temperatures. This

reduction would also result in a defect UO_2 lattice, but in addition,

it would release oxygen to the composite causing an increase in the

oxygen activity of the system. Based on the results of screening tests

on partially-clad composites, further study will be made of fully-clad

composites containing fuel particles stabilized with either PrO_2 or CeO_2

solid solution additions.

SUMMARY

In selecting a fuel-matrix system for fuel elements in a tungsten,

water-moderated reactor, prevention of fuel losses due to both fuel

vaporization and decomposition must be considered. The various

methods for reducing fuel losses must take into account the properties of the composites and the various fabrication and inspection methods available for tungsten-uranium dioxide fuel elements. Based on these considerations and the current knowledge of fuel stabilization, tungsten-coated uranium dioxide particles containing 10 mole % yttria have been selected for use in fabricating the initial generation of configurations that will be used in an extensive fuel element testing program. This combination of fuel-stabilizer and vaporization-inhibitor should result in tungsten-uranium dioxide composites with acceptable fuel retention capabilities under the currently envisioned reactor operating conditions. However, since more severe reactor operating conditions (i.e., higher temperatures and/or longer lives) may eventually be required, study of other methods of reducing fuel losses is continuing.

REFERENCES

1. Lietzke, Armin F.: Water-Moderated Tungsten Nuclear Rocket Reactor Concept. NASA TM X-1044, 1965.

2. Gedwill, Michael A., Sikora, Paul F., and Caves, Robert M.: Fuel-Retention Properties of Tungsten-Uranium Dioxide Composites. NASA TM X-1059, 1965.

3. Watson, Gordon K.: Fabrication of Thin Tungsten-Uranium Dioxide Composite Plates. NASA TM X-1073, 1965.

4. Gedwill, Michael A.: Investigation of Some Variables Affecting and Some Method of Reducing Thermal-Cycling Fuel Losses from W-UO_2 Composites. Proposed NASA Technical Memorandum.

5. Garfinkle, Marvin: Effects of Additives on Thermal Stability of Tungsten-Uranium Dioxide Composites. NASA TM X-1118, 1965.

6. Gluyas, Richard E., and Gedwill, Michael A.: Stabilization of $W-UO_2$ Composites Under Thermal-Cycling Conditions. Proposed NASA Technical Memorandum.

7. Buzzard, Robert J., and Gill, Frank L.: High-Temperature Mechanical Properties of a Tungsten-Uranium Dioxide Composite. NASA TM X-1018, 1964.
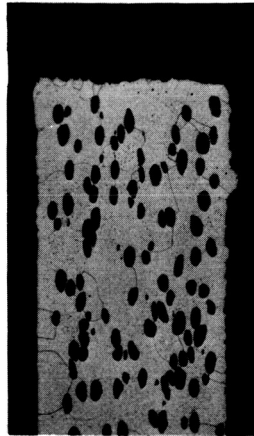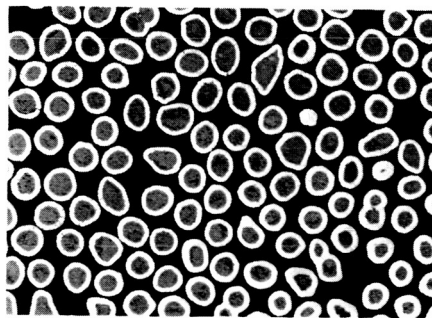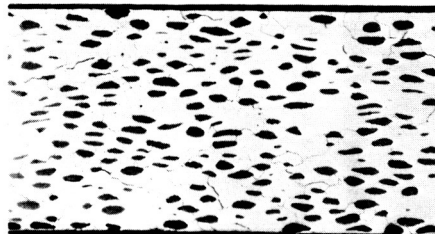
E-3068

Fig. 1. - W + 20 volume % UO$_2$ composite surface clad by vapor deposition and tested for 2 hours at 4500° F in H$_2$.

(a) Containing less than 50 ppm of halide.

CS-31146

(b) Roll composition tested.

Fig. 2. - Use of tungsten-coated UO$_2$ particles in producing UO$_2$ composites.
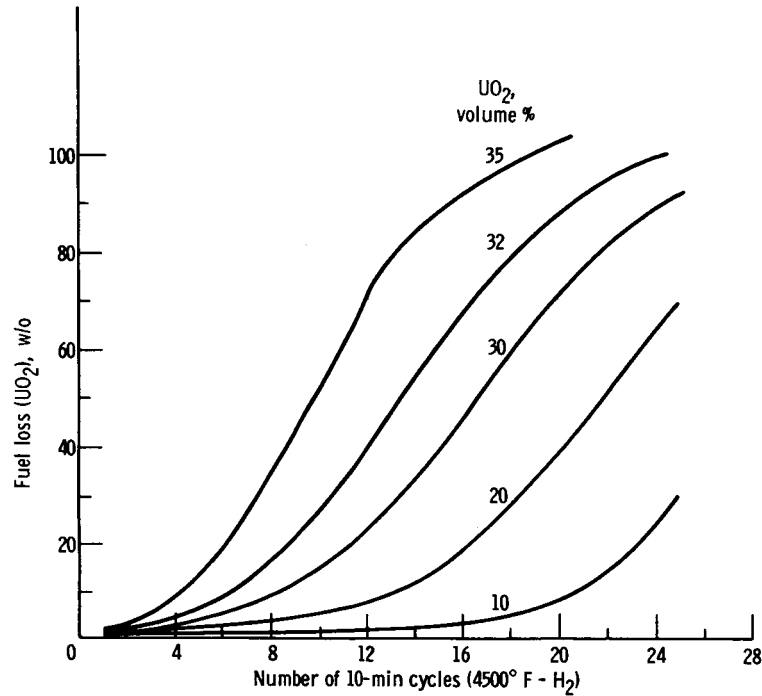
Fig. 3. - Effect of fuel loading on fuel loss from thermal cycled W-UO$_2$ specimens. (Sample size, $1\frac{3}{8}$ by 1 by 0.021 in.; approx. 0.002 in. tungsten cladding on major faces; edges unclad; fuel particle size, approx. 50 μ.)
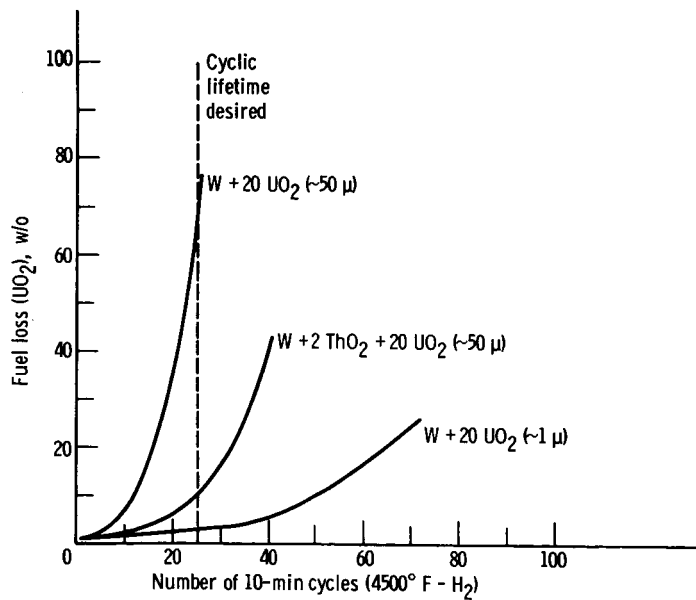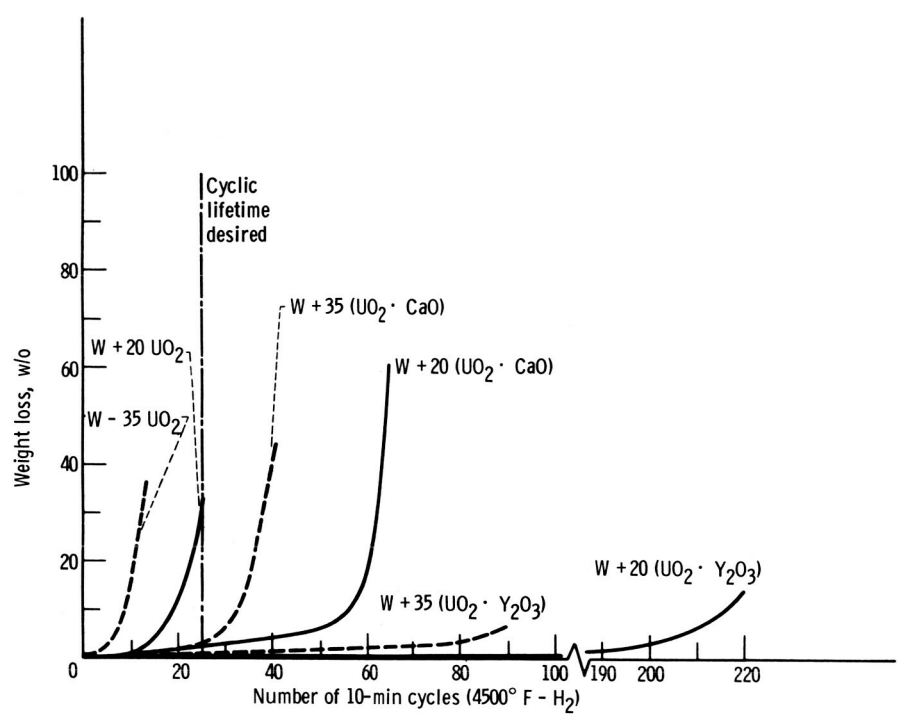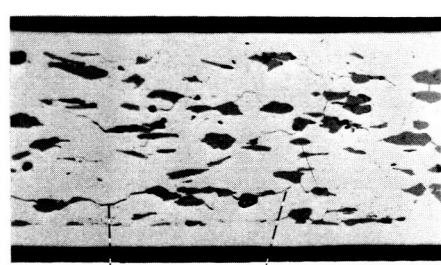

Fig. 4. - Effect of either ThO$_2$-additions or fine UO$_2$ particles on the thermal cycling life of W-UO$_2$ composites. (Sample size, $1\frac{3}{8}$ by 1 by 0.021 in.; approx. 0.002 in. tungsten cladding on major faces; edges unclad.)
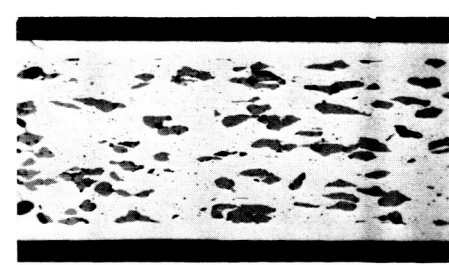
E-3068

Fig. 5. – Effects of stabilizing additives on the thermal cycling life of fully clad W-UO$_2$ composites. (Sample size, $1\frac{3}{8}$ by 1 by 0.021 in.; approx. 0.002 in. tungsten cladding on major faces and >0.050 in. tungsten cladding on edges; additives, 10 molar % additions in solid solution with UO$_2$; fuel loadings expressed in volume % as equivalent UO$_2$ concentrations.)

UO$_2$ containing 10 molar % CaO   UO$_2$ containing 10 molar 70 Y$_2$O$_3$

Fig. 6. – W + 20 (UO-X) composites tested for 25 10-minute cycles to 4500° F in H$_2$.
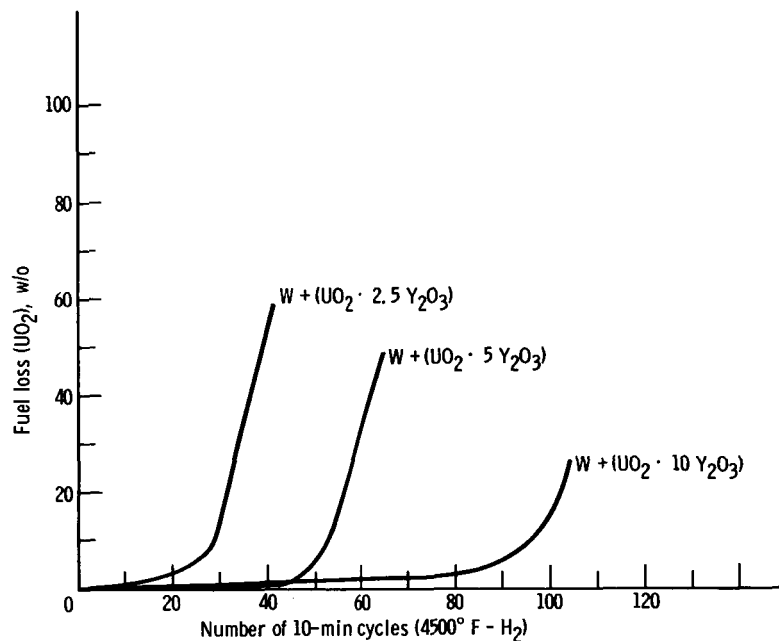
E-3068

Fig. 7. - Effect of varying amounts of Y_2O_3 additions on the thermal cycling life of fully clad $W-UO_2$ composites. (Sample size, $1\frac{3}{8}$ by 1 by 0.021 in.; approx. 0.002 in. tungsten cladding on major faces and >0.050 in. tungsten cladding on edges; additives, Y_2O_3 additions expressed as molar % in UO_2; fuel loadings, uranium content equivalent to $W + UO_2$ composites with 35 volume % UO_2.)